

~~Description~~  
~~Microstructured Gas Sensor with Gas-Sensitive Properties Controlled by~~  
~~Imposition of an Electric Field~~ **MICRO-STRUCTURED GAS SENSOR WITH CONTROL**  
**OF GAS SENSITIVE PROPERTIES BY APPLICATION OF AN ELECTRICAL FIELD**

**PRIORITY INFORMATION**

This application claims priority from German application 102 10 819.6, filed March 12, 2002 and International application PCT/EP03/02544 filed March 12, 2003.

**BACKGROUND OF THE INVENTION**

The invention relates in general to gas sensors and in particular to a microstructured gas sensor having gas sensitive properties that are controlled by application of an electric field according to the features of the preamble of Claim 1.

~~Such m~~Microstructured gas sensors are disclosed for example in German published patent applications DE 44 42 396 A1 and DE 195 44 303 A1.

~~—~~In recent years, resistance-type ~~resistive~~ gas sensors have been increasingly used to measure air pollutant concentrations in the ppm and ppb ranges. ~~The main a~~Advantages of such semiconductor gas sensors include relatively is their low manufacturing cost along combined with the simplicity of hybrid integration into electronics for the conditioning of the measured signals~~ments~~. Semiconductor gas sensors are typically electrical conductance or resistance sensors. At operating temperatures of 50 °C to 900 °C, the electrical resistance of the semiconductor film changes upon contact with the gas to be for detected~~ion~~. This reversible reaction makes possible the electronic detection of a gas. Typical detected gases may be ~~are~~ NO<sub>x</sub>, CO, hydrocarbons, NH<sub>3</sub>, O<sub>3</sub>, and H<sub>2</sub>O. Both the electrode structures and the gas-sensitive films of

these sensors ~~may are typically be manufactured fashioned chiefly by~~ thick-film and thin-film methods. Common materials for the active sensing elements ~~may include are semiconductoring~~ metal oxides such as<sup>†</sup>  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Cr}_2\text{-}_x\text{Ti}_x\text{O}_3$ , etc., and organic semiconductors ~~such as (polypyrrole, polyaniline, and phthalocyanine)-[1]. Here~~†The temperature ~~may is~~ usually ~~be~~ employed to control the chemical reaction on the semiconductoring films.

In these sensor arrangements, heaters and temperature sensor structures ~~may are~~ usually ~~be~~ integrated on a suitable substrate platform. The gas sensitive metal oxide films ~~such as for example  $\text{SnO}_2$  may are then be~~ deposited on such platforms by thick-film and thin-film methods. Concentration of heat development by the heater ~~may be is~~ concentrated on the sensitive surface with the aid of microstructured substrate platforms, while the surrounding region can remain cold. ~~It may thus be This is~~ advantageous for example ~~in order to~~ locate the detection electronics on the cold part of the substrate-[2]. Thermal decoupling ~~may be is~~ effected for example with thin membranes of  $\text{SiO}_2/\text{Si}_3\text{N}_4$  or so-called-hotplate structures-[3].

Semiconductor gas sensors, for example (metal oxide sensors,) are based on the relatively (simplified) functional principle that gas molecules are adsorbed at semiconductor surfaces and a certain portion of them may enter into a chemical bond with the semiconductor (i.e., chemisorption). Electrons ~~may be are~~ localized and /bound in the semiconductor-adsorbate complex or may be liberated by it. In the band model of the semiconductor, this corresponds to occupation of a surface state (with electrons or holes) that ~~must~~, in terms of its energetic position, is to be localized near the Fermi energy in the band gap-[4].

Because the bound charge carriers are no longer available for current transport, this reoccupation of surface states ~~may is~~ usually ~~be~~ detected with conductance sensors. An

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† A comma was probably intended after  $\text{Ga}_2\text{O}_3$ .—Translator.

approximately equivalent option for measurement, so far not utilized in industry, comprises surface potential sensors (e.g., SGFET) [5, 6]. ~~A The central disadvantage of the known arrangements of these sensors (e.g., SGFET) is that no design takes into account the planar manufacturing methods of conventional semiconductor fabrication.~~

The reoccupation of surface states results in a shift in the energy levels (i.e., position of the Fermi level). This in turn has retroactive effects on the surface states themselves, because the energy levels available are now differently distributed. This is why, for example, only a portion of the adsorbed gas molecules can go over to the chemisorbed state, because the occupation probability of the surface state is diminished along with the position of the Fermi level under chemisorption (self-blocking, “Weisz effect”) [7].

~~Further~~ ~~What is more,~~ from the principles of semiconductor electronics it is known that the position of the Fermi level can be affected not just by the temperature and doping but also by electric fields. In gas sensors of the prior art, the position of the Fermi level ~~may be is determined~~ through the temperature; ~~in the gas sensor described and illustrated hereinafter the position of the Fermi level may be present invention it is determined~~ through electric fields. This is also known as “electroadsorption.” If, therefore, an electric field is impressed on a gas-sensitive semiconductor surface, the resulting shift in the Fermi level ~~brought about in this way~~ makes it possible to control the adsorption probability (chemisorption and physisorption) of gases on these surfaces. Gas sensors can therefore be made subject to electrical modulation of their sensitivity to various gases. In this way a parameter for gas sensors, which may be adjustable with no power consumption, becomes available such that the sensitivity modulation can be substantially expanded in terms of response time and selectivity through the heater temperature.

This electroadsorptive effect was postulated by Fedor Wolkenstein in 1957[8]. Because it requires very high electric fields (close to the dielectric breakdown strength of air), however, it was not until 1968 that Hoenig and Lane\_, ~~after great experimental effort,~~ experimentally confirmed the occurrence of the effect on a zinc oxide film placed in a flat-plate capacitor[9].

The potential inherent in this electrical sensitivity control of micro-structured MST2-gas sensors ~~has been~~ was immediately recognized in the prior art. by these groups [10, 11, 12] and manifested itself in a rather large number of patent applications for such sensors; up to now, however, no

What is needed is a gas sensor ~~has been developed~~ whose design is oriented to the vertical electrical controllability of its sensitivity.

## **SUMMARY OF THE INVENTION**

~~The invention pursues the goal of a~~An improved gas sensing technology through the use of the electroadsorptive effect with small and low-cost sensors ~~that can find use in, among other fields, production and process metrology, automobile manufacture, safety engineering, and climatic and environmental monitoring.~~ The gas sensing technology described and illustrated herein invention makes it possible to implement semiconductor gas sensors with relatively markedly better properties than prior art sensorsheretofore. In particular, the gas sensor may have relatively according to the invention is to have enhanced selectivity and may be capable of functioning at lower operating temperatures, for example~~that is,~~ significantly below 300 °C.

~~This goal is achieved with a microstructured gas sensor having the features of Claim 1.~~

~~— Developments of this gas sensor are identified in the dependent claims.~~

The invention is based on gas sensors described and illustrated herein functioning on the basis of gas-sensitive semiconductor materials. In contrast to known gas sensors made of semiconductor material, in which a change in resistance in the resistor film is typically sensed ~~read out solely by two electrodes~~, in the sensor ~~s~~ according to the invention there may be ~~are~~ additionally at least one electrode, and ~~but~~ advantageously a plurality of electrodes inside the semiconductor body of the gas sensor for controlling the ~~sensitivity~~ activity. This ~~(t)These~~ further electrode(s) ~~is~~ may be ~~(are)~~ located under the resistor film and may be ~~are~~ isolated from the resistor film ~~it~~ by an insulator film. This ~~(t)These~~ further electrode(s) ~~serve s~~ (serve) to produce an electric field acting on the semiconductor. The effect of the electric fields on the gas reaction of the sensitive film may be ~~is~~ utilized ~~here~~. To this end, ~~it is necessary that an electric field produced in the semiconductor body of the gas sensor via a field electrode may be is effective up to the surface of the gas-sensitive film that faces toward the gas. That is to say, the films lying above the gate electrode do must not screen the electric field.~~ The Debye length  $L_D$  is a measure of the shielding length in semiconductors. ~~According to the invention, t~~The insulator film located between the resistor film and the further electrode(s) may have ~~has~~ a maximum thickness that is ~~at least approximately less than or approximately equal to~~ approximately ten ~~10~~ times the Debye length of the insulator material employed. The thickness may be ~~is~~ preferably chosen to be ~~approximately less than or equal to~~ three ~~3~~ times the Debye length, and the thickness may further be ~~is especially preferably chosen to be~~ less than or equal to this Debye length.

The Debye length  $L_D$  may be ~~is here~~ defined as follows:

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2 Presumably *Mikrosystemtechnik*, hence — microsystems technology; but it is possible *Mikrostrukturiert* (= microstructured, micromachined) was meant. — Translator.

$$L_D = \sqrt{\frac{\epsilon\epsilon_0 kT}{q^2 N}}$$

where

T is the temperature,

$\epsilon$  is the relative permittivity of the material,

$\epsilon_0$  is the absolute permittivity,

k is the Boltzmann constant,

N is the charge-carrier concentration and

q is the elementary charge.

In the case of the frequently used gas-sensitive material SnO<sub>2</sub>, for example,  $L_D$  is approximately 60 to 80 nm. The screening length in insulators may be relatively large—is ~~theoretically very great~~. In an implementation in a real component, however, impurities or defects and interfacial states may mean that the thickness of the insulator film does ~~should~~ not exceed 300 nm, so that a sufficiently strong electric field can still be produced in the sensitive material of the gas sensor.

~~Preferably, a~~ plurality of further electrodes may be ~~are~~ arranged in the semiconductor body, which ~~(question: is the semiconductor body everything or not?)~~. This fashioning, which is ~~preferably but not necessarily employed with the above mentioned sizing of the insulator film,~~ makes it possible to offset or ~~control in a wholly purposeful way~~ the gradient in the surface potential variation due to the potential drop between the two electrodes of the resistor film.

The sensors ~~may according to the invention~~ comprise semiconductor materials (such as for example the metal oxides<sup>3</sup>  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Cr}_{2-x}\text{Ti}_x\text{O}_{3+z}$ , etc., or organic semiconductors) under which one or more further electrodes, called field electrodes ~~in what follows, are~~ may be deposited, these field electrodes being isolated by an insulator film.

The ~~sensors may be arrangements according to the invention are~~ distinguished by, among other things, the fact that they are structured on the substrates customary in microelectronics (such as silicon and silicon dioxide). What is more, it ~~may is also be~~ possible to build on other substrates customary in gas sensing technology such as  $\text{Al}_2\text{O}_3$  (including sapphire) in its usual forms.

In addition, ~~It is particularly expedient to employ, between the control electrode and the semiconductor, an insulator material~~ may be utilized that can withstand a high breakdown field strength and which does not screen electric fields. ~~The following improvements and advantages in comparison with the known art can be cited with the gas sensor according to the invention:~~

Conventional gas sensors are operated at high temperatures of 250 °C to 900 °C (~~reason: to control absorption; see above~~). In contrast, ~~With the arrangement according to the sensors described and illustrated herein invention,~~ the operating temperatures can be reduced to values below 200 °C.

The sensor arrangement ~~may according to the invention is expected to~~ yield an improved selectivity of the sensor for a target gas through utilization of the electroadsorptive effect.

The advantages of a low operating temperature may be ~~are made still more~~ evident by the possibility of integrating CMOS processing electronics on the sensor chip.

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<sup>3</sup> A comma was probably intended after  $\text{Ga}_2\text{O}_3$ . The expression “3 + z” in the last subscript in the list is as in the original. —Translator.

The sensor arrangements ~~as described above~~ can be operated as an integrated sensor (~~e.g., a dosimeter~~) through utilization of the electroadsorptive effect.

A kinetic effect can also be introduced by modulating the gate voltage. Operation with a time-varying gate voltage periodically shifts the Fermi level in the metal oxide, that is, alteration of the electrochemical equilibrium under the effect of an external voltage on the field electrode. Periodic modulation of the gate voltage leads to an alternating variation in the resistance of the sensitive film. Through spectral analysis of this alternating variation in resistance, it may be ~~appears possible~~ to associate distinct frequency components with distinct gases and thus to achieve a gain in selectivity.

The possibility exists of electrical desorption of adsorbed gases, which can be driven away from the surface of the sensitive film by a strong field pulse. In this way an initial state of the sensors may be ~~is~~ restored during continuous operation (i.e., baseline zeroing).

~~A further possibility (as an alternative to the finger electrode structure,)~~ a further possibility for bringing about the lateral distribution of the field under the sensitive film may be ~~to provide is to fashion~~ the control electrode as a resistor, so that the potential drop along the resistor as current flows through it is parallel to the (~~intended~~) variation in surface potential of the sensitive film.

A combination of sensor temperature variation with field control may be ~~is~~ possible.

Alternative operating modes of the controllable sensor in the linear/active region of the thin-film transistor may be ~~are~~ possible.

Further alternatives include a ~~An~~ adaptation of the finger electrode width to the grain size of the sensitive material, where ~~with the optimum that~~ each finger may drives one grain (~~or a few grains,~~) or that the spacing of finger electrodes may be ~~is~~ in the range of the Debye length of the



sensitive material or, alternatively, a finger electrode width that is less than or equal to the Debye length of the sensitive material. ~~In what follows, the invention is explained on the basis of exemplary embodiments with reference to the drawings, in which:~~

These and other objects, features and advantages of the present invention will become more apparent in light of the following detailed description of preferred embodiments thereof, as illustrated in the accompanying drawings.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

~~FIG. figure 1 is a cross section schematic representation of the mode of action of a gas-sensitive sensor and an accompanying graph illustrating the potential variation in the sensor according to the invention;~~

~~FIG. figure 2 is a cross section of depicts an first embodiment of the gas sensor of FIG. 1 with a single field electrode located in the semiconductor body;~~

~~FIG. figure 3 is a cross section of depicts an second embodiment of the gas sensor of FIG. 1 with a plurality of field electrodes located in the semiconductor body; and~~

~~FIG. figure 4 is a cross section of depicts a CMOS thin-film gas sensor with control electronics in a sectional view.~~

### **DETAILED DESCRIPTION OF THE INVENTION**

~~Referring to The main idea of the invention (see FIG. figure 1,) is the following: If one has a gas sensor includes an electrode 1 disposed under a gas-sensitive semiconductor film 3 with and an insulator layer film 2 in between; then tThe aforementioned electroadsorptive effect may can occur when only if the thickness of the gas-sensitive semiconductor film 3 is onf the order of~~

the Debye length  $L_D$ . In this way the surface absorption of gas molecules 4 can be controlled through an electric field. ~~Further, What is more, care must be taken that the insulator layer 2 may be is-low in defects because these defects can substantially shorten the Debye length of the insulator layer 25 and thus interfere with penetration~~ of the field to the gas-sensitive film 3. Examples of Debye lengths for  $\text{SnO}_2$  are ~~for example 60-~~ 80 nm;<sup>4</sup> ~~where for a real insulators these lengths may be are-~~ in the range below several micrometers.

~~Referring to FIG. figure 2, is a sectional view of a first exemplary embodiment of the gas sensor according to the invention. There is the gas sensor includes~~ a semiconductor substrate 1 on which is disposed a gas-sensitive film 4 with a thickness of for example 59 nm-lies. Theis gas-sensitive film 4 may be is-contacted by two electrodes 5. The gas-sensitive film 4 can be made for example of  $\text{SnO}_2$ . The Debye length of this gas-sensitive film 4 may be is-approximately 80 nm. Below this gas-sensitive\_film 4 there may be disposed is-a field electrode 2 isolated by an insulator film 3.

Theis field electrode 2 may be provided is-fashioned as a plate electrode with and has-its entire area located below the gas-sensitive film 4. The insulator film 3 may have has-a thickness of for example 200 nm;<sup>4</sup> ~~†The Debye length of the gas-sensitive this-film 4 may be is~~ approximately 300 nm if silicon oxide is employed as the material for insulator film 3.

A measure for the screening length in semiconductors may be the is-the already mentioned-Debye length  $L_D$ , which is given by:

$$L_D = \sqrt{\frac{\epsilon \epsilon_0 k T}{q^2 N}}$$

<sup>4</sup> The original has 60.80 nm. —Translator.

Thus, in the case of the frequently used gas-sensitive material  $\text{SnO}_2$ , the Debye length  $L_D$  ~~may be is~~ approximately 60 to 80 nm. ~~A The above mentioned~~ thickness of approximately 200 nm for ~~the~~ insulator film 3 ~~helps to ensure makes certain~~ that a sufficiently strong electric field can be produced in the semiconductor via ~~the~~ field electrode 2.

~~A further embodiment of the gas sensor according to the invention is depicted in~~ Referring to FIG. ~~figure~~ 3, ~~in contrast to the gas sensor of FIG. figure 2, there is now a plurality of~~ microelectrodes 6 ~~disposed~~ under the gas-sensitive film 4, ~~may be provided~~ instead of a single field electrode 2.

———The use of such microelectrodes 6 spaced apart from one another has ~~the following an~~ advantage ~~in that~~. ~~The~~ gas-sensitive properties of a semiconductor film depend on the surface potential and thus the position of the Fermi level of the surface of gas-sensitive film 4 facing toward the gas. This effect ~~may be is~~ utilized in the ~~gas sensor illustrated in FIG. 3 present case~~ for controlling the sensitivity and selectivity. ~~In order to~~ To utilize this effect, ~~in optimal fashion, it~~ ~~may be is~~ desirable to have a constant potential over the entire semiconductor surface of the gas-sensitive film 4.

If a voltage is applied to ~~the~~ electrodes 5 ~~in order to~~ read out the resistance of ~~the~~ gas-sensitive film 4 ~~from the to~~ electrodes 5, a potential drop ~~may~~ appears between the two electrodes 5 and thus a gradient ~~may~~ appears in the surface potential. By applying various voltages to ~~the~~ microelectrodes 6, ~~which are separate and which are fashioned separately from one another,~~ electrically isolated from one another and located under ~~the~~ gas-sensitive film 4 inside ~~the~~ semiconductor substrate 1, it ~~may be is~~ possible to compensate ~~for~~ this gradient and thus set a constant potential on the semiconductor surface or shift the potential in desired directions.

Referring to FIG. 5, the gas sensor ~~may~~ The arrangements according to the invention have ~~at their disposal~~ a heater (see Figure 4) for the required working temperatures, which ~~may be~~ are above 100 °C. The chip in which the gas sensor is embodied ~~may need to~~ must be heated to over 100 °C, because ~~adsorbed~~ water on the surface of the gas-sensitive film 4 ~~may will~~ otherwise hinder the gas reaction. ~~The~~ is resistive heater ~~may can, as depicted in Figure 4,~~ be buried in the substrate 1 or structured on the surface. Because the sensitivity of semiconductor gas sensors ~~may~~ be ~~is~~ a function of temperature, it is especially favorable if the heater can be controlled ~~and/or~~ regulated. To this end, it ~~is desirable to integrate on the sensor chip~~ may have a temperature sensor whose signal can be used to acquire the actual temperature.

The gas sensor arrangement ~~may according to the invention~~ appears particularly expedient for ~~reducing~~ the operating temperatures of conventional semiconductor gas sensors (250-900 °C) to values below 180 °C. For this reason, integration of CMOS drives electronic circuits on the sensor chip ~~may be~~ is possible as a particular embodiment. ~~Figure 4 shows the schematic structure of a gas sensor with CMOS driver electronics according to the invention~~

## VI—References

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Although the present invention has been shown and described with respect to several preferred embodiments thereof, various changes, omissions and additions to the form and detail thereof, may be made therein, without departing from the spirit and scope of the invention.

What is claimed is: